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Volatile Halocarbon Production from the Chlorination of Marine Algal Byproducts, Including D-Mannitol

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■ The ability of various exudates of marine algae to produce chloroform during solution chlorination was investigated. D-Mannitol generated amounts that increased markedly with increase in pH, whereas glycerol under similar conditions yielded little product. L-Proline exerted an inhibiting effect. The mechanism of the D-mannitol reaction is believed to proceed via formation of a ketolactone which undergoes ring opening by chloride, followed by the classical haloform process.

The generation of volatile halocarbons during chlorination of aqueous environments has been demonstrated for both fresh (*1–3*) and marine waters (*4–6*). Investigations into the chemical nature of the precursors responsible for their generation have disclosed that in addition to the natural humic substances initially proposed by Rook (*7*) and later studied by Stevens et al. (*8*), various other organic compounds may also function as haloform precursors (*9*).

In a previous study (*6*), chlorination of estuarine water containing cultured marine algae revealed that the resulting concentrations of volatile halocarbons were dependent upon the species of algae. For example, in the presence of 10^6 cells/mL of *Isochrysis galbana* (Chrysophyceae), chlorination increased the concentration of volatile halocarbons normally generated in estuarine water by 41%. The presence of *Thalassiosira pseudonana* (Bacillariophyceae) resulted in a 24% decrease, whereas populations of *Carteria* spp. (Chlorophyceae) did not produce a statistically significant difference in the concentration of volatile halocarbons. Further, chlorination of the same estuarine water after removal of algal populations by filtration resulted in volatile halocarbon concentrations similar to those produced when algal cells were present, suggesting that the production of these compounds may be attributed to chlorination of specific metabolic byproducts of the algal species.

Hellebust (*10*) reported that glycerol, mannitol, and proline were excreted singularly or in various combinations by 81% of the marine algal species examined and generally comprised between 50 and 90% of the total identified exudate. Therefore, these three compounds were selected as models for the following study of the chlorination of algal byproducts.

Experimental Section

Chlorination of each model compound was performed in triplicate with molar ratios of compound to chlorine of 1:3, 1:1, and 3:1. Stock solutions (0.1 M) of glycerol, D-mannitol, and L-proline were prepared from "Fisher Certified" grade reagents (Fisher Scientific Co) and carbon-filtered, deionized water (Continental Water Conditioning). Individual aliquots of stock were pipetted into two sets of 12 100-mL glass volumetric flasks. Solutions in two flasks were buffered at pH 7 with a phosphate buffer while the remaining flasks were treated with appropriate volumes of 0.1 M NaOH to furnish the desired concentration of added hydroxide ion. All were then diluted and chlorinated with aqueous NaOCl (Fisher Scientific Co) to give final concentration ratios of model compound to chlorine (Cl^+) of 0.003:0.009, 0.003:0.003, and 0.009:0.003 with added OH^- concentrations of 0.0 (pH 7), 0.003 (pH 10.8), 0.006 (pH 11.2), and 0.009 M (pH 11.4) at each ratio. Both sets of flasks were stoppered with Teflon-lined screw caps and left under overhead fluorescent lighting (2500 lm/m^2) at 20 °C. Aliquots (2 mL) were taken from each flask of one set at 10, 30, 60, and 180 min, then randomly thereafter for 24 h and added to a beaker containing 1 mL of acetate buffer (pH 4) and 2 mL of freshly prepared 20% KI solution (Fisher Scientific Co). The mixture was diluted to 200 mL with carbon-filtered deionized water and amperometrically analyzed for total residual oxidant as given in Standard Methods (*11*). Residual oxidant determinations were performed with a Wallace and Tiernan amperometric titrator. Phenylarsine oxide titrant (0.0056 N) was obtained from Wallace and Tiernan Co.

After 24 h, residual chlorine oxidants in the remaining set of flasks were quenched by adding 5% $Na_2S_2O_3 \cdot 5H_2O$ (1 mL) (Baker Analyzed Reagent). Contents of the flasks were immediately extracted with 2 mL of pesticide grade pentane (Burdick and Jackson Laboratories, Inc). A 1.0-μL aliquot of the organic layer was then removed with a microliter syringe for gas-chromatographic analysis of total volatile halocarbons. Gas chromatograms were obtained with a Hewlett-Packard Model 5710A gas chromatograph with a ^{63}Ni electron capture detector. A 1.8 m × 2 mm i.d. glass column packed with 12% OV-101 on Anakrom Q 101/120 mesh (Analabs, Inc) was used. Injection port and detector temperatures were 100 °C. The column was maintained at 55 °C, and 95:5 argon/methane used as the carrier gas (40 mL/min). Identification of the major chromatographic peaks was made by employing the admixture technique to extracted samples. Quantification was accomplished by direct comparison of sample peak areas to those of authentic standards in pentane.

Results and Discussion

In the absence of added hydroxide ion (pH 7.0), only L-proline demonstrated a chlorine demand significantly different (Student's t test, $\alpha = 0.05$) from the deionized water blank (Table I). While volatile halocarbons were not detected from the reaction, molar ratios of L-proline to Cl^+ of 3:1 caused rapid reduction of oxidative Cl^+ from the nominal 110 mg/L to 6 mg/L in 10 min and to a nondetectable residual (<0.01 mg/L) after 180 min. Introducing hydroxide ion to aqueous solutions of L-proline had no effect on the inability of this compound to generate haloforms during chlorination. Even with a nominal excess of Cl^+ of 3:1, chlorine residuals were

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Table I. Average (N = 3) Residual Chlorine Concentration (in mg/L) with Time in the Absence of Hydroxide Ion (pH 7) from Model Compound Solutions (0.009 M) Chlorinated with NaOCl to a Nominal 110 mg Cl^+/L (0.003 M)

sample	0 min	10 min	60 min	180 min	1440 min
blank H_2O	110	110	112	108	100
glycerol	110	108	108	107	101
D-mannitol	110	108	108	106	100
L-proline	110	6	1	<0.01	<0.01

Table II. Average (N = 3) Total Volatile Halocarbons (in μg/L) Produced in the Absence of Hydroxide Ion (pH 7.0) from Model Compound Solutions Chlorinated with NaOCl

sample	0.003 M sample + 0.009 M Cl^+	0.003 M sample + 0.003 M Cl^+	0.009 M sample + 0.003 M Cl^+
blank H_2O	5 ± 2	3 ± 2	3 ± 2
glycerol	4 ± 3	4 ± 2	8 ± 3
D-mannitol	7 ± 4	10 ± 4	6 ± 3
L-proline	2 ± 1	<1	<1

completely reduced after 24-h contact with L-proline without concurrent production of volatile halocarbons.

Because of its greater reactivity leading to N-chlorination (*12*), proline can, in addition, apparently inhibit the generation of volatile halocarbons during the chlorination of natural waters. Our estuarine water, which normally produces an average of 187 μg/L of bromoform and chlorodibromomethane when chlorinated, generated only 85 μg/L after addition of 0.003 M L-proline. Although we were unable to identify any proline/chlorine reaction products, Smith (*13*) demonstrated, using high-performance liquid chromatography, that the addition of up to a 3:1 molar excess of NaOCl to solutions of proline in seawater from Biscayne Bay, FL, produced an unknown product which he proposed was possibly 2-bromopyrrolidine.

At all three molar ratios of model compound to chlorine employed, the volatile halocarbon concentrations produced during the chlorination of glycerol and D-mannitol solutions buffered to pH 7 were not statistically different (Student's t test, $\alpha = 0.05$) from the carbon-filtered deionized water blank (Table II). However, with the addition of hydroxide ion, D-mannitol exhibited a discernible increase in reactivity. Regression analysis showed highly significant linear correlations (P <0.001; 95% confidence level) between increasing nominal hydroxide ion concentrations and the concurrent increases in both chlorine demand (Figure 1) and production of volatile halocarbons (Figure 2). Total halocarbon comprised mainly chloroform with lesser amounts (16–61 μg/L) of one unidentified product and traces (<0.1 μg/L) of a third unidentified compound. Greatest haloform production was observed when D-mannitol was in excess. At the D-mannitol/chlorine ratio of 3:1, the yield of total volatile halocarbons was 557 μg/L following chlorination in the presence of 0.009 M hydroxide ion. This represents an increase of 450% from the mannitol/chlorine ratio of 1:3 in the presence of 0.009 M hydroxide ion. In addition, glycerol exhibited no significant (Student's t test, $\alpha = 0.05$) change in halocarbon yield as pH increased (Figure 3). These results correlate nicely with the fact that the presence of *Isochrysis galbana*, whose principal exudate is D-mannitol (*10*), increases the chloroform concentration in surrounding waters during chlorination, whereas *Thalassiosira pseudonana* and *Carteria*, which secrete mainly proline and glycerol (*10*), respectively, have a negative or little effect.

Polysaccharides have been identified as widespread components of natural waters (14–20), but they do not make up the principal category of the organic matter. Fulvic acids represent the bulk of the carbon-containing material (*20, 21*). From a previous study involving certain members of the series, the conclusion was drawn that sugars, in general, do not appear to be significant precursors of chloroform, nor do they contribute to chlorine uptake (*9*). In view of the present results, it appears that in terms of potential for haloform production there is specificity in relation to the type of sugar and the reaction conditions, especially pH.

We present here a mechanistic sequence that serves to ra-

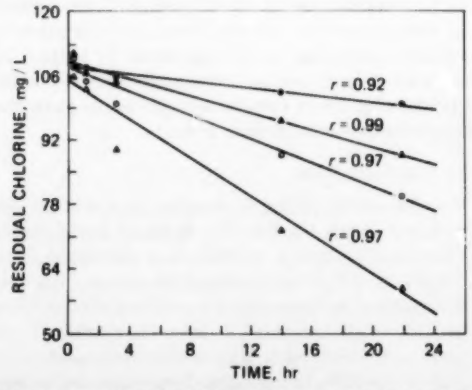


Figure 1. Total residual chlorine as a function of time for solutions of D-mannitol (0.009 M) containing nominal 0.0 (●), 0.003 (▲), 0.006 (○), and 0.009 M (△) OH^- as NaOH. Solutions were chlorinated with aqueous NaOCl to a nominal 0.003 M Cl^+ at time zero.

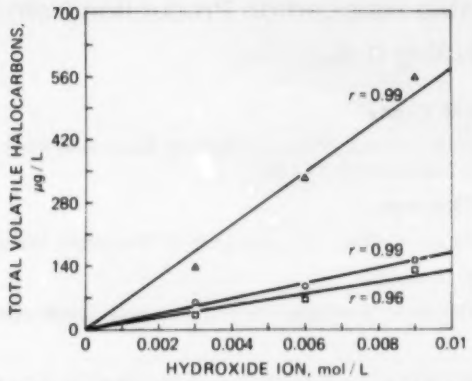


Figure 2. Total volatile halocarbon production as a function of nominal hydroxide ion concentrations as NaOH added to solutions of D-mannitol/Cl of 0.003:0.009 (□), 0.003:0.003 (○), and 0.009:0.003 (△).

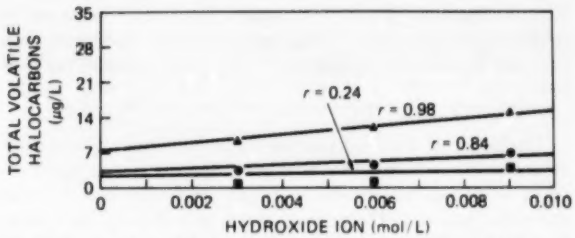


Figure 3. Total volatile halocarbon production as a function of nominal hydroxide ion concentrations as NaOH added to solutions of glycerol/Cl^+ of 0.003:0.009 (■), 0.003:0.003 (●), and 0.009:0.003 (▲).

tionalize the chloroform product from mannitol, as well as other aspects of our experimental data. The haloform reaction provides a unifying theme, together with other transformations which are reasonably expected to occur under the conditions employed. The structural prerequisite of the haloform reaction is a ketone capable of trihalogenation at the α-carbon, a situation absent from the constitution of all common sugars, including D-mannitol.

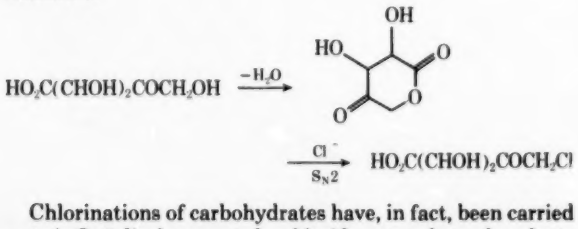
The presence of hypohalite, however, readily produces oxidative derivatives of carbohydrates, as appreciable previous work has shown. For example, common oxidation products of polyols in the presence of NaOBr or NaOCl are hydroxyketones and hydroxyketo acids, some of which may exhibit carbon chain shortening via loss of carbon dioxide (*22a–c, 24a,b,e*). (Enzymatic oxidation can also take place in natural waters (*22d*).) By analogy, D-mannitol might reasonably be expected to undergo the oxidative degradation depicted (Scheme I). Because of its structure, however, the oxidation product is incapable of trihalogenation at the α-carbon, owing to the hydroxyl substituent's extremely poor leaving capabilities in nucleophilic reactions. It is, therefore, unlikely that haloform production can occur directly from these hydroxyketone intermediates.

Scheme I

$$HOCH_2(CHOH)_4CH_2OH \xrightarrow{NaOCl} HO_2C(CHOH)_2COCHOHCO_2H \xrightarrow{-CO_2} HO_2C(CHOH)_2COCH_2OH$$

Further reactions common to these systems provide a possible key to the production of volatile halocarbons. Since characteristic behavior of oxidized sugars in aqueous solution is lactonization to form 5- or 6-membered rings (*22e*), a structure (Scheme II) in which the methylene α to the ketone is attached to the carboxylate functionality could easily arise, providing a far better leaving group than hydroxyl in S_N2 displacements. We propose that chloride ion (small concentrations of which are generated in chlorinated waters from HCl arising in the oxidation process or from salt normally present in natural water) acts as a nucleophile upon the ketolactone to produce α-chlorinated keto acids, analogous to attack of lactone by cyanide (*23a*).

Scheme II



Chlorinations of carbohydrates have, in fact, been carried out via S_N2 displacements by chloride on tosylate, phosphate, and nitrate esters (*24f*). In ordinary aliphatic systems, chloride displacement of the nitrate group has an activation energy of 27.5 kcal/mol, whereas the corresponding reaction of carboxylate ($\approx F$) requires ~29 kcal/mol (*25, 26a*). This represents a 16-fold decrease in rate of displacement. The ketone α to the methylene, however, lowers the activation energy of the process by at least 6 kcal/mol, and more probably by 7 or 8 kcal/mol. This has been demonstrated in experiments in which S_N2 displacement rates of chloride from chloropropanone and 1-chloropropane were compared (*26b*). Since the present system entails carboxylate displacement by chloride, whereas the system referenced (*26b*) comprises chloride replacement by iodide, the ketone probably enhances the rate here by 1 or 2 kcal/mol more than it does in the cited experiment. This is because the transition state of S_N2 displacement receives greater stabilization from the carbonyl when the nucleophile and leaving groups are poorer, as they are in our system. (Identical *A* values are assumed for the rate calculations.) The presence of the keto moiety allows the transformation to proceed at a minimum of 2100 times (possibly as much as 160 000 times!) the rate of chlorinations of nitrated sugars. Furthermore, steric hindrance to attack is less in the lactonic system than in the open-chain analogue, a situation which should further increase the rate. Theoretically, both γ- and δ-lactones could be involved in this process, although the appropriate γ derivatives are opened with considerably greater difficulty than their δ counterparts (*22e*).

Generation of the α-chloroketo acid is followed by the haloform reaction (Scheme III). It is well-known that the rate-determining step in such a process is formation of the enolate anion (23b).

Scheme III

$$HO_2C(CHOH)_2COCH_2Cl \xrightarrow[OH^-]{NaOCl} HO_2C(CHOH)_2COCCl_3 \xrightarrow{OH^-} HCCl_3 + HO_2C(CHOH)_2CO_2H$$

Various correlations can be made between the schematic outline and the following experimental findings with the D-mannitol model system: the rate of chlorine uptake increased appreciably with increases in hydroxide ion concentration, and a threefold drop in the concentration of Cl^+ did not significantly affect the rate of haloform production over a range of hydroxide ion concentrations, whereas a threefold increase in the concentration of D-mannitol did so markedly. For example, the required preliminary oxidations are more rapid and extreme at higher pH (*24b*); the haloform reaction is base catalyzed and is terminated by attack of hydroxide at the carbonyl group. These features of our proposal correlate with previous findings that haloform production during chlorination of drinking water is known to be greatly increased at higher pH values (*27*). It should be noted, however, that other organic components of natural waters, including the major ones, have been shown to yield chloroform upon addition of hypohalite (*20, 21*).

Green's finding (*24c*) that inulin, the polysaccharide of D-fructose, yielded bromoform, oxalic acid, and glycolic acid when treated with bromine water is noteworthy since a sequence similar to the one described above, including lactonization, could be invoked to account for the products. Furthermore, it is significant that our data show that glycerol, which is incapable of forming a γ- or δ-lactone, did not exhibit enhanced chloroform production with increases in hydroxide ion concentration (Figure 3). On the other hand, glycerol can function as a precursor to haloform under acid conditions, as shown by the production of bromoform, glyceric acid, and carbon dioxide on exposure to bromine water (*24d*). Presumably, the sequence in Scheme IV pertains. This pathway may also apply to the D-fructose–Br_2–H_2O system (vide supra).

Scheme IV

$$HOCH_2CHOHCH_2OH \xrightarrow{(O)} HOCH_2COCH_2OH \xrightarrow{H^+} HOCH_2COCH_2OH_2^+ \xrightarrow[-H_2O]{Br^-} HOCH_2COCH_2Br \xrightarrow[\text{reaction}]{\text{haloform}} HOCH_2CO_2H + HCBr_3$$

A number of simpler mechanistic proposals have been made on systems where acetyl, rather than hydroxyacetyl, groups act as precursors for chloroform in the classical haloform reaction during chlorination of natural waters (*9*, *28–30*). Evidence in some cases indicates the presence of a trichlorinated intermediate that hydrolyzes to produce chloroform under alkaline conditions (*9*). The polyol precursors that we discuss here require a somewhat different approach because the hydroxyl groups complicate the structural requirements.

Finally, it should be noted that the postulated reactions need not be efficient, high-yield processes since the haloalkanes are formed in extremely small amounts.

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